<table>
<thead>
<tr>
<th>Title</th>
<th>WHO WAS TAFEL?</th>
</tr>
</thead>
<tbody>
<tr>
<td>Author(s)</td>
<td>MÜLLER, Klaus</td>
</tr>
<tr>
<td>Citation</td>
<td>JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 17(1): 54-75</td>
</tr>
<tr>
<td>Issue Date</td>
<td>1969-04</td>
</tr>
<tr>
<td>Doc URL</td>
<td><a href="http://hdl.handle.net/2115/24891">http://hdl.handle.net/2115/24891</a></td>
</tr>
<tr>
<td>Type</td>
<td>bulletin</td>
</tr>
<tr>
<td>File Information</td>
<td>17(1)_P54-75.pdf</td>
</tr>
</tbody>
</table>
WHO WAS TAFEL?

By

Klaus Müller*

(Received December 30, 1968)

Abstract

TAFEL, active in Würzburg from 1885 to 1910, was a pupil of Emil FISCHER with whom he worked on carbohydrates. In 1898, during work on the structure of strychnine, TAFEL found his famous method of reducing electrolytically substances otherwise hard or impossible to reduce. He extended this to many classes of compounds, some of industrial importance, but also investigated the electrode processes. He proposed the mechanism (now known as TAFEL mechanism) of catalytic hydrogen atom combination as rate-determining step in electrolytic hydrogen evolution, originated quantitative methods to observe overpotential and the course of electrolytic reactions, including methods for preparing active electrodes (activation) and for solution purification (pre-electrolysis), and found the logarithmic relation between current density and overpotential (now known as Tafel law).

The story of TAFEL's life, which ended in tragic illness, is told as a story of the beginnings of modern electrochemistry.

Introduction

Fifty years ago, at the age of only 56, a man whom we should know and remember as a founder of modern electrochemistry, Julius TAFEL, ended his agonizing illness in death. His name has become an adjective in the language of every electrochemist concerned with electrode reactions, and much of his work is remembered in monographs on organic electrochemistry; yet he is one of the unknown men in our science. The reasons for this are open to speculation: Is it because of the stronger personalities of a NERNST, OSTWALD, or HABER who were his contemporaries? Is it because of his early retirement? Or is it perhaps because the name of his great teacher Emil FISCHER the organic chemist was so firmly attached to all the important compounds studied by TAFEL the organic chemist turned electrochemist?

In my attempts to find out about TAFEL, his work with FISCHER, his own work, and about his pupils, I have come to regret that our science of electrochemistry has no chronicle, for electrochemistry cannot be indexed by

*) American Cyanamid Co., Stamford, Conn. 06904, U.S.A.
Who was Tafel?

short formulas, and its history cannot be traced in lists of Nobel laureates.

My warm thanks are due Professor Horiuti who asked me the crucial question. The outcome of the search I dedicate to him.

TAFEL’s early years

Julius Tafel was born\(^a\) in Switzerland (Choindez, Canton Berne, 2 June 1862); he attended the Realgymnasium (a secondary school with scientific direction) at Stuttgart and Nürnberg. From 1880 he studied in Zürich, München, and Erlangen. In Erlangen, he started to work as an assistant of Emil Fischer who had assumed a professorship there in 1882, and who recognized early\(^b\) the young, talented chemist, and in 1884, Tafel produced his dissertation on the isomerism of indazole and (the hypothetical) isindazole under the guidance of Fischer (indazole had just been discovered by Fischer and Kužel). Together with Paal\(^{2,3}\) Tafel worked briefly on syntheses of heterocyclic compounds, a field in which Ludwig Knorr began to earn fame there and then.

When in the fall of 1885 Fischer transferred to Würzburg, less then 100 km west of Erlangen, Tafel, together with Knorr, followed him as private assistant, and in due course produced a Habilitationsschrift (1888) in which he worked out a particularly simple route to amines consisting in the reduction of the phenylhydrazones of aldehydes and ketones (phenylhydrazine, of course, was Emil Fischer’s first great discovery that enabled him to make his great advances in carbohydrate chemistry).

Fischer’s private laboratory consisted\(^b\) of a simple living room, and an adjacent office for consultation had to be used for weighing and optical experiments, yet over the next years, the very difficult experiments in carbohydrate synthesis were carried out in these rooms. Fischer had a large number of co-workers in this enterprise; Tafel he mentions in the first place, and describes\(^b\) how, in the first synthesis of an hexose (acrose), he and Tafel, using the technical means available at the Farbwerke Meister, Lucius, and Brüning at Hoechst, prepared for several weeks great quantities of acrolein and of acrolein dibromide, an operation done in the open and on windy days exclusively, and how Tafel once inadvertently happened into a cloud of the biting acrolein fumes, with the consequence of extremely severe nose bleeding. But of course this important early work\(^{10-17}\) on the carbohydrates was the foundation of Fischer’s success in the continued work in this field, and his award of the Nobel Prize in 1902 (for this and the work in the purine group). On 23 July 1890 when Fischer reported first about the early work before the Presidium of the Chemische Gesellschaft in Berlin,\(^1\) Tafel carried out the experimental demonstrations.
For this participation in Fischer's work Tafel, of course, had had to interrupt the progress of his own, independent work which had started so brilliantly with his devising the above-mentioned method of producing amines (treating the hydrazones with sodium amalgam and glacial acetic acid in alcoholic solution); there was also the unfortunate entry of Goldschmidt who quickly captured Tafel's reduction method in its obvious application to the oximes\(^b\). Thus Tafel, to further his academic career, had to find another novelty, since he resented no doubt any kind of polemics or public controversy, commonplace though as they were then; and he chose, perhaps in connection with his own work on amines, or just as likely since it was the compound used (see, for example, Ref. e) in the separation of racemic mixtures into optically active components, to investigate the alkaloid strychnine, along with its companion and analogue in physiological effect, brucine. This was the first attempt at elucidating the structure of these alkaloids, which during Tafel's lifetime had not been resolved completely.

In the fall of 1892, Fischer went to Berlin, and in his words,\(^b\) "a professor of chemistry migrates not merely with his scholarship and books, but also with preparations, apparatus, and assistants". [Note that sequence.] For the assistants W. Wislicenus and Tafel however, (Knorr had left for Jena in 1889), there were no fitting vacancies in Berlin, and so they remained in Würzburg.

That university was a great centre of scientific activity indeed, and it may
be appropriate here to mention the succession of great chemists and physicists on the chairs. In chemistry, after Emil Fischer (1882–1892) there was Arthur Hantzsch (1893–1903, thereafter in Leipzig) who worked on the oximes and diazo compounds, and whom we owe much in the way of introduction of physical methods into organic chemistry, and of recognition of the existence of time factors; he was succeeded by Tafel (1903–1910) who in turn was succeeded by Eduard Buchner (1911–1917) who in 1907 had received the Nobel Prize for his work on fermentation. A similarly stellar succession we
find in physics: There was Friedrich Kohlrausch (1875–1888) who became famous for his “Lehrbuch der praktischen Physik”; Wilhelm Konrad Röntgen (1888–1900) who discovered the X-rays in Würzburg, which won him the first Nobel Prize for physics ever awarded; and Wilhelm Wien (1900–1920) who also won a Nobel Prize for physics for his work on heat radiation, and who with his assistant (and later successor) Friedrich Harms edited the Handbuch der Experimentalphysik. Also in Würzburg was the Professor of Physiology Adolf Fick (1868–1899) who formulated the famous laws of diffusion.

Both Fischer and Hantzsch had the greatest misgivings when they left Würzburg, for here they had spent very happy and very successful years, in fact the happiest of their lives, as they would realize later. Hoesch\textsuperscript{f} writes that “for most academic people Würzburg appears as one of those places which, like Bonn and Heidelberg, comprise a microcosm of completeness… Academic traditions and social intercourse could unfold at natural ease and as a friendly matter of course”: a very friendly city, with many fortunate external factors contributing to the well-being of university life (among which the Würzburger beer still is better known to the outside world than the commended local wines). In spite of this, says Fischer, one could not complain about lack of enthusiasm among students and co-workers.

All this contrasts with the given conditions: “A small annex and a little-inviting basement room”\textsuperscript{f} were Fischer’s laboratory, and much of the work was not only difficult but also a hazard to health. Fischer had improvised hoods installed, and taken steps that a new institute was built in the mid-nineties, but it may well be that Tafel’s health was broken before then, for there are clear breaks in his publishing activities, and there is mention of interruptions due to ill health starting from March 1894\textsuperscript{46} (Fischer himself had a chronic phenylhydrazine poisoning, and in 1903/04 suffered from insomnia). We might doubt, therefore, that Tafel took more than a passive part in the non-scientific activities at Würzburg University, of which Fischer gives a vivid example. Every year there was a play enacted, and (probably around 1892) this was in form of an operetta, “The Chemikado”, fashioned with the melodies of Sullivan’s “Mikado” that had just appeared, and with a humorous text by Dr. Reitenstein, one of the assistants. Costumes and wigs were borrowed from the municipal theatre. In the title role there was Alfred Maurit, Fischer’s nephew, Tafel’s pupil and later director of the Dortmunder Aktienbrauerei, wearing Fischer’s laboratory suit and hat, speaking Fischer’s Low-rhenish dialect, and thus coming all the more into prominence among the “Japanese” crowd in the plot.

Tafel’s own scientific work until 1898 centered on strychnine\textsuperscript{25,27,28,32,46,50,51}
and amino compounds; and while his publications then hardly indicated it, TAFEL turned away from pure organic chemistry in this period and indeed became a physical chemist. His lectures between 1888 and 1893 concerned organic chemistry, including the chemistry of dyes, alkaloids, heterocyclic and isocyclic compounds. But from 1893 on, he lectured mainly on general and physical chemistry, including an "Experimentalvorlesung". (Later, when he had become ordinarius, he read experimental chemistry and also about quantitative analysis.)

TAFEL's first publication in physical chemistry (by no means then a field represented widely by chairs at universities) came in 1896, after he had spent some time with Wilhelm OSTWALD in Leipzig. There he must have seen work on electrolysis; in any event, using lead cathodes, TAFEL succeeded in 1898 to reduce strychnine, i.e., to replace one and both of its oxygen atoms by hydrogen, a reaction that had not been achieved with any other reduction method available then, including TAFEL's own reduction with sodium amalgam. TAFEL could thus show that both the oxygen-containing rings in the molecule contribute to the poisonous, spasm-producing action of strychnine, and that in fact the presence of two groups acting in the same sense in the same molecule is responsible for the eminent poisoning effect, which TAFEL himself checked in frog experiments.

The discovery of the superior reducing effect of lead cathodes was a milestone in chemistry as well as an important stimulus to the work of TAFEL who in that year, 1898, was named professor, since what now followed was a singular outburst of activity, in a spirit of discovery and significance, yet comprised of work carried out meticulously—in "aller Gründlichkeit", an example of a carefully developed advance into new territory. A new period in TAFEL's career had begun.

The electrochemical period

While there had been periods of illness and apparent inactivity in the years between 1892 and 1898, a great period of activity followed the successful reduction of strychnine in 1898, culminating in the years 1902/03 when TAFEL was able to present summaries and experimental illustrations of his work on a variety of substances and substrates to the 9th Meeting of the German Electrochemical Society (Würzburg, 9/10 May 1902) and to the Physical-Medical Society of Würzburg (22 January 1903). Also in 1902, he had become extraordinarius, and in 1903 ordinarius and director of the chemical institute, and from 1903, married, he also lived in very happy personal circumstances.)
K. MüLLER

It did not take TAFEL any appreciable length of time to lay the foundations of his electrochemical work. Already in 1900 all the main ideas were published,26 following presentation of the work during the Naturforscherversammlung in Munich 1899 (“On the course of electrolytic reductions”). When TAFEL summarised his work again in 1906,27 as an invited review of his own work in the Zeitschrift für Elektrochemie, nothing principally new had to be added.

What TAFEL wrote in 190026 need only be stressed in 1968. (And note especially what TAFEL tells us in footnotes.) First, how did he know that a reduction was successfully proceeding? “For this investigation I have worked out a procedure which allows one to observe, conveniently and under the same conditions as in expedient preparative use of the electrolytic reduction, whether a reduction [footnote: or oxidation] does set in, and how it proceeds”. The principle of this method was to put in series with the reaction vessel a hydrogen coulometer and to compare the quantities of hydrogen evolved in the two vessels. ELBS8 had actually developed an analogous procedure earlier, and in effect observed quantitatively reduction kinetics, however, not only had his paper been rejected by the Chemische Gesellschaft for the Berichte, an act typical for the attitudes prevailing at that time toward the time factor in chemical reactions, but apparently ELBS had not developed this in a more lasting way thereafter, and the value of the method came only to the fore in TAFEL’S hands in his observations on hard-to-reduce substances.

Next, then, when were reductions successful? Lead or mercury had to be used, and a host of disturbing influences had to be excluded: “For the reduction of caffeine, the course of reduction was found reproducible only if every trace of foreign metal was carefully excluded from the cathode chamber.” This included such traces as were present in many organic preparations, or in most commercial lead samples, and material dissolving from the anode. When TAFEL added various metals to the catholyte, he realised that already 0.04 mg of platinum (in a cell typically of 330 cc capacity, with a cathode of 100 cm²) sufficed to halt reduction completely. [Footnote: this quantity, if deposited evenly, corresponds to a layer merely 2 Å thick]. In their disturbing action, the metals were found to be Pt > Ag > Sn > Cu > Hg > Zn > Fe. Small disturbing effects could be removed by addition of lead acetate which would form an electrode deposit; but if the electrolytic solution contained more disturbing traces of foreign metals, TAFEL recommended to change the cathode after 15 min, lifting the old one out of the solution without interrupting the current. He thus originated pre-electrolysis. TAFEL also realised that disturbing metals such as platinum readily dissolve anodically, either from
Who was Tafel?

a platinum anode, which therefore must be avoided, or from an old lead cathode which had been used in connexion with a platinum anode and was thus “thoroughly infested” with platinum. He introduced the use of special-quality lead into organic preparative chemistry; but he also put the disturbances to good use. In a footnote, we read: “This can be used as a simple method for determining the cathodic overpotential. A given cathode is put opposite a lead anode that is sufficiently oxidised. A given current is passed and constancy of the potential difference is awaited. Then, platinum solution is added to the catholyte. The current is regulated to be the same as before, and the new potential difference is noted. Assuming that the platinised cathode has the same overpotential as platinum itself, the overpotential of the cathode is then known”. (This created the basis of his eminent work of 1905.80,81)

Tafel’s admonition: “Use of platinum anodes, therefore, represents great danger in all work concerning polarisation”,82 has gone unheeded for six decades: platinum often is used in all confidence ever since in 1899 Nernst’s pupil Caspari1) had stated that “platinum befits a special position in electrolytic respects, not only because of its freedom from attack, but also because of its extraordinary reversibility”.

Thirdly, Tafel outlined the pre-treatment of cathodes: “Far safer and more convenient than chemical methods of cathode preparation is the electrolytic preparation”, and went on to describe a prior anodic treatment, so as to cover the lead cathode with lead superoxide, followed by a cathodic treatment, if possible just prior to the reduction operation proper, so that a spongy, active surface is obtained.

Why, finally, were lead and mercury successful cathode materials? Tafel concluded that a reduction will only be achieved when the overpotential at the cathode reaches a certain value; lead and mercury, according to Caspari,1) have the highest overpotential. A competition between the reduction, say, of caffeine:

\[ C_8H_{19}O_2N_4 + 4 H^+ = C_4H_{12}ON_4 + H_2O + 4 e \]  

I

and hydrogen evolution:

\[ 2 H^+ = H_2 + 2 e \]  

II

was postulated, with reaction I occurring measurably only when II is relatively slow, and “therefore overpotential values in a given solvent for II are a direct measure of the probability of I as compared to II, even if nothing is known about the reaction rate of I”. Again in a footnote, we read: “Probably reaction II is a composite reaction and consists of \( 2 H^+ = 2 H + 2 e \) and \( 2 H = \)
K. MÜLLER

\( \text{H}_2 \); and then in the main text: “It should be assumed that the existence of the ‘cathodic overpotential’, qualitatively as well as quantitatively, is connected with the combination of \( 2 \text{H} \) to \( \text{H}_2 \), and this in fact because of a different catalytic action of metals on this process, which in the case of platinum is particularly strong”.

Thus, in this single paper\(^{56} \) we have the basic elements of modern views on electrocatalysis, surface preparation, pre-electrolysis, and the qualitative as well as quantitative aspects of electrochemical kinetic research. But something else, I feel, is significant in this paper. This is the complete absence of the term ‘depolariser’, so much used in TAFEL’s day and even now. For one, TAFEL’s strychnine and caffeine were hardly “depolarising” an electrode; but then, TAFEL substituted the superior concept of competition, and laid open the electrode as a catalyst.

Many reductions had been achieved before Tafel, nitrocompounds being the favourite objects of study, and the aspects and achievements of this research were splendidly presented by HABER in 1898.\(^{k) \} \) The limitation of this work was its application to the reversible situation, therefore, insight in the catalytic aspects, the effect of cathode material, and the nature of the effect of electrode potential was restricted, and theoretical conclusions could not go beyond the connexion with the Nernst equation.

It will not appear so unusual, therefore, that the TAFEL equation was not discovered by NERNST’s school in Berlin or OSTWALD’s in Leipzig, but in that single room at Würzburg University; and in retrospect, it seems fitting that the 9th Meeting of the German Electrochemical Society was held in Würzburg in 1902. (It was, incidentally, just there that the Society decided to become known as Bunsengesellschaft für angewandte physikalische Chemie.) Among the participants of that meeting, we find BILLITZER (later BILLITER; Göttingen), BODENSTEIN and OSTWALD (Leipzig), ELS (Giessen), FOERSTER and E. MÜLLER (Dresden), HABER and Le BLANC (Karlsruhe), H. J. VAN’T HOFF (Amsterdam), J. H. VAN’T HOFF (Berlin), HITTORF (Münster), LÖB (Bonn), R. LUTHER (Leipzig), NERNST (Göttingen), ZSIGMONDY (Jena) and W. WIEN (Würzburg). The president, J. H. VAN’T HOFF, in greeting the session on its opening, expressed especial thanks in behalf of the society to Prof. TAFEL for his gift of electrochemical preparations for the HOFMANN House, the Berlin headquarters of the Chemische Gesellschaft; these included campidine, desoxy-theobromine and hydroxylamine hydrochloride.

In his talk at the meeting TAFEL stressed\(^{72} \) the difference between his and CASPARI’s overpotential determinations, in that he had chosen the high current densities necessary for practical work, rather than the very low current
Who was Tafel?

densities which Caspari had used to define his overpotentials (cf. the decomposition potentials defined before by Le Blanc\(^1\)). We cannot help feeling, however, that Tafel's presentation did not carry over too well. Tafel did not dwell on the kinetic relations found by him but rather discussed complicated phenomena of activation and "depression", or passivation as we would call it to-day, and he did not excel in the discussion with Bodenstein and Nernst who made him admit to "depolarising effects". The lecture had something of a preliminary tone, and we must wait for the publication in 1905 of his work on overpotential and reduction of organic compounds that filled an entire issue of the Zeitschrift für physikalische Chemie.\(^{80,81}\)

In the meanwhile, Tafel had done another beautiful piece of physical chemistry, this time following a lead given by W. Wien. The latter had, in the Würzburg meeting, lectured about "positive electrons", and put forward arguments that canal rays are positive ions. Tafel had prepared zinc oxide for these investigations, and there were several problems which were "too chemical" for Wien, whereupon Tafel studied the fluorescence of zinc oxide under the influence of canal rays. The results he interpreted with the conclusion that the fluorescence is due to intrinsic properties, and not due to impurities, as maintained by others. Tafel\(^{77,78}\) was right.\(^m\)

Those 1905 papers mentioned above \(^{80,81}\) spelled out clearly that the definition of overpotential is only meaningful when the current density is given as well. It was found that with metals such as Pb, Cd, Ag, and Cu, activation and depression states may be exhibited, depending on the polarisation history of the electrode, possible access of anolyte, chemical and time factors; some metals attained maximum polarisation at a given current density quite slowly. A table of overpotential values was given, which became a classical reference, and for Hg as well as approximately for Pb and Cd, it was found that (with Tafel's symbols)

\[
\varepsilon = a + b \log J
\]

(1)

where \(\varepsilon\) is the polarisation, \(a\) and \(b\) are constants, and \(b=0.107\), increasing with temperature; \(J\) is the current density. In the kinetic derivation of the numerical value of \(b\), the well-known discrepancy was found, i.e., the cathode potential on Hg and Pb was increasing much faster with current density than it should according to theory (that is, by the Tafel mechanism). Tafel adduced Haber and Russ' work\(^a\) to explain this as a deviation from the gas law: "The hydrogen modification forced to accumulate in the cathode boundary layer, therefore, should obey, not the laws of dilute but rather those of concentrated solutions. This appears plausible, in particular for one who prefers to
take the viewpoint that he has to deal with an accumulation of atomic hydrogen or a labile hydrogen compound whose concentration can without argument be assumed as large". Thus, additional work is required for continued H₂ evolution, and a deviation from the value as derived from the NERNST equation must be expected.

JAHN and SCHÖNROCK⁵ had, in fact, derived Eq. (1) from thermodynamic considerations, and JAHN⁶ had given experimental proof. HABER⁷ finally had argued that this was a result required by the NERNST equation. But TAFEL thought that this could only be so when “certain assumptions about the anodic polarisation hold, and I therefore consider the direct experimental proof given with my tests as not superfluous”. With this statement, in fact, electrode kinetics for the first time appeared separate from thermodynamics, allowing irreversible reactions to be studied systematically. Since TAFEL stressed the overriding importance of current density, he turned attention to electrode reactions as a rate process, as it would be called later, and not as an appendix of the NERNST electrode potential. In the same sense, he dispensed with the “so-called absolute potential”, and referred overpotentials to the reversible hydrogen electrode.

There were other, scattered results about the logarithmic law (Eq. (1)) available prior to 1905 but TAFEL’s ample discussion and meticulous experimental execution on a wide range of materials single his work out as the chief advance, and Eq. (1) carries his name with full justification.

Among the results of TAFEL and NAUMANN⁸, the logarithmic relation between efficiency for reduction and cathode potential was in principle a confirmation of HABER’s work, with the difference of course that the object of reduction in TAFEL’s work were substances that were hard to reduce, a fact permitting him to notice (i) that catalysis also takes place with respect to the organic substance, since caffeine was reduced more rapidly on mercury, succinimide more rapidly on lead, the overpotentials on these metals being equal; (ii) that this catalytic effect is smaller in magnitude than that on hydrogen evolution; (iii) that both hydrogen evolution and the reduction reaction at the cathode are entirely coordinated, irreversible reactions, and that the cathode potential arises because of the necessary accumulation of hydrogen in some form in the cathode boundary layer. Even earlier, TAFEL had found⁹ strong catalytic effects of the cathode metal on reduction, and had stressed that the electrolytic reduction effect on a given cathode material may differ qualitatively as well as quantitatively from the chemical reduction effect of the given material; thus both Cu and Hg give rise to NO formation when brought in contact with HNO₃ in the gas phase, while during electrolysis, NH₃ is produced.
Who was Tafel?

on copper, and NH$_2$OH on mercury. “Therefore, one must speak of a specific reduction effect of a given cathode.” Thus electrocatalysis was defined, if not named.

In the above-mentioned review there is also a clear exposition of Tafel’s view that “the existence of cathodic overpotential is thus due to differences [between various metals] in the rate of hydrogen gas formation”; cathodes with the smallest overpotential accelerate most strongly hydrogen evolution. We read that the phenomenon resides in the surface layer, and that even a hydride layer will strongly affect catalysis. Interesting further the observation that “with investigations at high current densities one also gains the advantage of stirring by hydrogen evolution, an effect not produced by any other means of stirring to the same extent”.

With a certain dose of resentment Tafel and Naumann wrote: “Haber as well as Löb have carried out their experiments with substances that are readily reduced, even after one of us had shown that electrolytically reductions can be realised which are not accessible in other ways”. For Tafel this meant, of course, that he had a wide-open field of research for himself. Already by the end of 1898 he had found that his reduction method worked, aside from strychnine, also in the cases of acyl amines (aromatic mainly—substituents proved to be important for the success or failure of a reduction), caffeine, and theobromine, and had developed the above method for quantitative study of the course of reduction. Other groups of organic substances followed in rapid succession, and his work found quick realisation in patents which we find issued in the name of C. F. Boehringer und Söhne in Waldhof near Mannheim: Reduction of xanthines (DRP 108 577; Ref. 53, 54), of camphoric acid imide (DRP 126 196; Ref. 68), of nitric acid (DRP 133 457 and 137 697; Ref. 73), and of oximes (DRP 141 346; Ref. 74, 75). Of these, the reduction of nitric acid to hydroxylamine gained particular economic significance, making this substance readily available for the first time. Tafel also succeeded with the first direct reduction of uric acid, and reduced many ketones, aldehydes, compounds with double bonds, etc. The wide range of Tafel’s achievements in preparative organic electrochemistry can best be seen from Fichter’s monograph.

Two finds require special mention. First, when acetone or methyl-ethyl-ketone were reduced on mercury or lead cathodes, metal alkyls were found to be formed, e.g., mercury-di-sec-butyl when methyl-ethyl-ketone was reduced on mercury. With lead, unsaturated alkyls could be obtained. This was one of the many pioneering studies in Tafel’s work, and the beginning of a field that commands great scientific and industrial interest today.
K. MÜLLER

Secondly, when acetoacetic esters were subjected to reduction, TAFEL succeeded to obtain hydrocarbons, a long-standing achievement; however, the hydrocarbons obtained did not exactly fit published physical constants. This turned out to be an unexpected anomaly known to-day as the TAFEL rearrangement.

Unfortunately, TAFEL’s health had been failing badly since about 1906, and when he realised this most interesting anomaly, his condition had already forced him into retirement at the age of only 48. He wrote in 1912 that this very interesting migration—he suspected, of the \( \text{CH}_3 \) group—during reduction of the carboxylic group in acetoacetic esters “should be followed up in various directions. I regret very much that external circumstances prohibit continuation of this work at present, but I hope that after some period of time I shall regain force and opportunity for the work”. It did not happen. Over 20 years later STENZL and FICHTER cleared up this difficulty with the rearrangement showing that the acyl group migrated.

TAFEL’s last publication, ironically, was in defence of his priority in the field of metal-organic compounds during electrolytic reduction.

The last years

TAFEL had fought his illness, he had hoped that his health could be restored through prolonged stays in spas, he had asked his pupils to his bedside even during fever spells, he had overstrained his forces during retreats of the illness, working until late in the laboratory, he had for years refused to live for his health. In 1910 finally, when his forces did not allow him to continue this fight, he asked for retirement, and went to Munich.

Far from ‘retiring’, however, he continued working, often in bed. His first desire was to remain useful to his science. Thus apart from helping those of his pupils who were still working on common problems, by correspondence and by receiving their frequent visits, he became extraordinarily active as a reviewer of books for the Zeitschrift für Elektrochemie. Between 1911 and 1918, more than 60 book reviews appeared, covering just about every imaginable field of chemistry: physical-organic chemistry, alkaloids, proof of constitution, experimental inorganic chemistry, caoutchouc and proteine chemistry, catalysis, organic analysis, electrochemical preparative chemistry, physical chemistry, chemical technology, history of chemistry, ferment. From these reviews, which were often very detailed, we gain once more insight into the concepts of this extraordinary mind. Again and again he regretted that the theory of reaction rate and chemical equilibrium had not found consideration in a book reviewed; elsewhere, that passivity phenomena were disregarded;
Who was Tafel?

then, of course, he criticised that reduction of organic compounds was seen merely as that of the nitrocompounds. He showed a clear predilection for experimental art, for kinetics, for the theories of organic chemistry, and stereochemistry. It is amply clear that he considered himself a physical chemist.

When his health appeared to improve, TAFEL set out to writing a textbook of organic chemistry which he wanted to put on an entirely new basis, making use of his rich experience in research and of his wide knowledge of the literature. He was not able to finish this task. His illness aggravated again, and in particular he was plagued by increased insomnia. His capacity to work collapsed, and he feared a complete nervous breakdown. He could not stand the idea that he would never again be able to work if his condition worsened, and so he died of his own hand on 2 September 1918.*

TAFEL's pupils

Among TAFEL's pupils or one-time assistants, three at least had distinguished academic careers: Otto Rosenheim⁹, who obtained his Ph. D. under TAFEL in 1892 and later became famous for his work on steroids; Bruno Emmert, who obtained his Ph. D. under TAFEL in 1905 and was Professor of Chemistry at Würzburg University from 1927-1951, doing important work on organic, especially heterocyclic, complexes; and Konrad Schübel, who was Professor of Pharmacology at the University of Erlangen 1924-1952.

Professor Schübel, who lives at Erlangen, has most graciously written to me about TAFEL when I asked him and what he says adds very importantly to our view of TAFEL and his time. Professor Schübel writes: "I was private assistant for one term in the chemical institute with TAFEL. He was then ill with tuberculosis, and during most of my stay there he was absent, undergoing treatments in Davos. On his request I worked on electroreduction of ketones. I had carried out the work by myself and done the elementary analyses, too. Professor TAFEL has acknowledged my support in a footnote".

Professor Schübel in fact is not evident as a co-author, and I wrote to him because of the footnote acknowledgments.⁹⁹-¹⁰¹ We must agree when he writes: "It is indeed difficult nowadays to understand this absolutist regime at universities 50-70 years ago". This certainly is not referred to TAFEL in particular. TAFEL was a very meticulous worker, and as much as he did not relent in his own efforts, he must have brought to bear similar expectations on his students, for Professor Schübel continues: "I recall that I wanted to attend a zoology lecture which I needed for my teachers' examination.
This course ran once a week from 6 to 8 p.m. Tafel did not consent, with the reasoning that in his laboratory work just about started around this time. He declared that I had enlisted into service with him and he expected me to put my entire strength into his service”.

For this reason, I have taken the unusual step, in the list of publications below, of citing co-workers even where they are not mentioned in the title. Certainly, most of the people listed do not reappear in the abstracted chemical literature later on. In fact, many students in Würzburg were medicine and pharmacology students, and a certain number no doubt became school teachers. Long scientific careers in industry I have been able to trace for Boerner, Hahl, Herterich, and Schepss in Germany, and for Houseman in America. E. P. Frankland became an accomplished novelist after he resigned from university teaching in 1920; Alfred Mauritz and Heinrich Günther became brewery directors. Moufang and Kann died at the time of graduation.

Emmert writes that many of Tafel’s pupils remained long in contact with him; among them were certainly Emmert himself, Schepss, and Renger. However, none of his pupils have continued working in the field opened by Tafel for more than a few years. Tafel’s work was not continued as such at Würzburg University, but certain aspects of his work have been picked up elsewhere. Thus Sakurai in Japan worked on the mechanism of phthalimide and succinimide reduction, and Fichter in Switzerland, apart from clarifying the Tafel rearrangement, extended this concept with a ring expansion, and tried to accomplish chemically some of Tafel’s reductions that had been possible so far only cathodically. He succeeded when using a sodium-lead compound, and wrote that “we now view the reason for the superior performance of the electrochemical method, not in the production of hydrogen by the current, but its arising at the lead surface, i.e., the delay of formation of molecular hydrogen from atoms by the lead”, with a reference to Bonhoff’s work. From the viewpoint of local-cell action, of course, this reduces to an elegant confirmation of Tafel’s work, rather than something chemically original. Last but not least there is the school of Professor Horiuti in Japan where Tafel’s conviction regarding a non-ideality factor in the Tafel constant is tested theoretically and experimentally.

**Tafel to-day**

Tafel’s contributions to electrochemistry cannot be summarised very briefly. His work touched off all the important developments in modern electrochemistry: the working in pure electrolytes, including pre-electrolysis and electrode preparation, the electrocatalytic aspects in terms of the Tafel
Who was Tafel?

mechanism of hydrogen evolution and of catalysis by surface layers in general, the quantitative study of irreversible electrode processes, in particular those involving hydrogen evolution and the reduction of organic substances that are hard to reduce, their consideration as competing reactions, and their kinetic treatment in terms of the TAFEL equation. Several of his detailed contributions had to be rediscovered later, some of his advice has not been followed yet, some has simply remained valid ever since he gave it. TAFEL has been the Emil FISCHER of electroorganic chemistry where his achievements gain perspective when we remember that in 1912, SABATIER was awarded the Nobel Prize for "methods of adding hydrogen to organic compounds".

TAFEL'S work is the more remarkable in view of his early retirement—retirement with the bitter realisation that he could not carry on with his creative work in electrochemistry. In later years he once singled out the motto: "Immer strebe zum Ganzen, und kannst du selber kein Ganzes werden, als dienendes Glied schliess an ein Ganzes dich an". This, if anything, summarises his Lebenswerk for us.

Added in proof. Dr. K. KOSCHEL, Würzburg, has kindly communicated excerpts from H. PAULY's unpublished memoirs. PAULY also observes that TAFEL, quite contrast to some other well-known organic chemists of his time, was most perceptive to modern theory (cf. pp. 66/67 above). Concerning the laboratory he writes: "TAFEL was very strict and meticulously accurate in directing the institute---Often he complained to me of the very scanty resources, yet he was reluctant to protest against these conditions. He downright sacrificed himself in the institute's service. Daily he concerned himself with every student in the organic laboratory. Already as Emil FISCHER's assistant he had worked much too hard, and later he was no longer equal to the exertions. On top of this there was the advancing illness."

Acknowledgments

Sincere thanks are due Prof. K. SCHÜBEL, Erlangen, and Prof. G. HARTMANN, Würzburg, for their very helpful information; also the Deutsche Bunsen-Gesellschaft, Frankfurt, and the British Information Services, New York.

References

a) B. EMMERT, Chemiker-Zeitung, 42, 481 (1918).
K. Müller

g) Akten des Rektorats und des Senats der Universität Würzburg, Nr. 857.
j) F. Haber, Z. Elektrochem., 4, 506 (1898).
   Chem., 26, 385 (1898).
q) F. Fichter, Organische Elektrochemie, Theodor Steinkopf Verlag, Dresden and
   Leipzig, (1942).
r) R. Galli, Chimica e l'Industria (Milano), 50, 977 (1968).
   846 (1937).
t) Z. Elektrochem., 17, 659-661, 785-788, 963 (1911), 18, 71-74 (1912), 19, 106, 158-159,
   538, 586 (1914), 21, 173-176, 306-307, 402-403, 589-590 (1915), 22, 119-120, 274-278, 363-
   259, 385 (1918).

Tafel's publications*

1) E. Fischer and J. Tafel: A. 227, 303-340 (1885)
   The hydrazines of cinnamic acid. II.
2) C. Paal and J. Tafel: B. 18, 456-460 (1885)
   Thiophene from mucic acid.
3) C. Paal and J. Tafel: B. 18, 688-689 (1885)
   Thiophene from erythritol.
4) J. Tafel: B. 18, 1739-1744 (1885)
   Benzoyl derivatives of phenylhydrazine.
5) J. Tafel: B. 19, 1924-1931 (1886)
   A new way of preparing primary amines.

* Abbreviations: A. = Liebigs Annalen der Chemie
                      B. = Berichte der deutschen chemischen Gesellschaft
                      ZE. = Zeitschrift für Elektrochemie
                      ZP. = Zeitschrift für physikalische Chemie

An asterisk marks electrochemical work.
Who was Tafel?

6) J. TAFEL: B. 19, 2414-2417 (1886)
About r-amino valeric acid. I.

7) J. TAFEL: B. 20, 244-249 (1887)
Reduction of diphenylhydrazine dihydroxytartaric acid.

8) J. TAFEL: B. 20, 249-251 (1887)
About r-amino valeric acid. II.

9) J. TAFEL: B. 20, 398-400 (1887)
Preparation of furfurylamine.

10) E. FISCHER and J. TAFEL: B. 20, 1088-1094 (1887)
Oxidation of polyvalent alcohols.

11) E. FISCHER and J. TAFEL: B. 20, 2566-2575 (1887)
Synthetic experiments in carbohydrate chemistry. I.

12) E. FISCHER and J. TAFEL: B. 20, 3384-3390 (1887)
Synthetic experiments in carbohydrate chemistry. II.

Isodulcitol. I.

14) E. FISCHER and J. TAFEL: B. 21, 2173-2176 (1888)
Isodulcitol. II.

15) E. FISCHER and J. TAFEL: B. 21, 2634-2637 (1888)
Oxidation of glycerol. I.

16) E. FISCHER and J. TAFEL: B. 22, 97-101 (1889)
Synthetic experiments in carbohydrate chemistry. III.

17) E. FISCHER and J. TAFEL: B. 22, 106-110 (1889)
Oxidation of glycerol. II.

18) J. TAFEL: B. 22, 1854-1860 (1889)
Reduction of hydrazones.

19) J. TAFEL: B. 22, 1860-1865 (1889)
About r-amino valeric acid. III.

20) J. TAFEL and A. NEUGEBAUER: B. 22, 1865-1867 (1889)
2-methyl pyrrolidine.

21) J. TAFEL: B. 22, 1868-1870 (1889)
Shaking apparatus for the laboratory.

22) J. TAFEL and C. ENOCH: B. 23, 103-108 (1890)
Alkylation of acid amides. I.

23) J. TAFEL and C. ENOCH: B. 23, 1550-1554 (1890)
Alkylation of acid amides. II.

24) J. TAFEL and A. NEUGEBAUER: B. 23, 1544-1550 (1890)
Dimethyl pyrrolidine and diamino hexane.

25) J. TAFEL: B. 23, 2731-2739 (1890)
Strychnine. I.

26) J. TAFEL and A. MAURITZ: B. 23, 3474-3475 (1890)
Phenacyl sulphide.

27) J. TAFEL (w. F. BOELSING): A. 264, 33-84 (1891)
Strychnine. I.
K. MÜLLER

   Strychnine. II.
29) J. TAFEL (w. I. VOGEL): B. 25, 412–413 (1892)
   A colour reaction of the acid anilides.
30) J. TAFEL (w. I. VOGEL): B. 25, 413–415 (1892)
   Acid hydrazides.
31) J. TAFEL (w. I. VOGEL): B. 25, 1619–1623 (1892)
   The oxidation of hydrogenated pyridines and quinolines.
32) J. TAFEL: B. 26, 333–335 (1893)
   The oxidation of strychnine.
33) J. TAFEL and I. VOGEL: B. 26, 335–337 (1893)
   The action of urea on nitrosamines.
34) O. ROSENHEIM and J. TAFEL: B. 26, 1501–1513 (1893)
   The oxidation of p-hydroxyquinoline.
   Isomeric diamino-succinic acids (butane-diamino-2,3-diacids).
   The behaviour of sodium peroxide towards acids.
   The oxidation of hydrogenated quinolines.
38) M. KANN and J. TAFEL: B. 27, 826–827 (1894)
   The oxidation of hydrogenated indoles.
39) J. TAFEL (w. SCHMIEDEL): B. 27, 2297–2306 (1894)
   The behaviour of sodium peroxide towards alcohol.
40) M. KANN and J. TAFEL: B. 27, 2306–2309 (1894)
   About α-phenyl ethylamine.
41) L. SENFTER and J. TAFEL: B. 27, 2309–2313 (1894)
   The γ-phenyl propylamine (amino-1α-propylbenzene) and its conversion into allyl-
   benzene (propenyl-1′-benzene).
42) L. SENFTER and J. TAFEL: B. 27, 2313–2314 (1894)
   About γ-amino valeric acid (amino-4-pentane acid) and methyl pyrrolidone.
43) W. BECKH and J. TAFEL: B. 27, 2315–2316 (1894)
   Diaz-aminobenzene.
44) H. GÜNTER and J. TAFEL: B. 28, 379–385 (1895)
   Isomeric 2,5-diamino-hexanes.
45) J. TAFEL: ZP. 19, 592–598 (1896)
   The so-called “indirect esterification”.
   Strychnine. III.
47) G. FENNER and J. TAFEL (w. F. SCHULZE): B. 31, 906–914 (1898)
   2-methyl-pyrrolidine.
   Reactivity of organic ammonium salts. I.
49) W. BRENDLER and J. TAFEL: B. 31, 2683–2686 (1898)
Who was Tafel?

Reactivity of organic ammonium salts. II.

50) N. MOUFANG and J. TAFEL: A. 304, 24-49 (1899)
Brucine.

51) N. MOUFANG and J. TAFEL: A. 304, 49-54 (1899)
Ethyl-strychnine and benzyl-strychnine.

*52) T. B. BAILLIE and J. TAFEL: B. 32, 68-77 (1899)
Reduction of acid amides to alkylamines.

*53) J. TAFEL (w. A. VEIT): B. 32, 3194-3206 (1899)
Desoxy-theobromine.

*54) T. B. BAILLIE and J. TAFEL: B. 32, 3206-3220 (1899)
Desoxy-caffeine.

*55) G. FENNER and J. TAFEL: B. 32, 3220-3228 (1899)
Anomalous composition of gold chloride double salts of organic bases.

*56) J. TAFEL (w. O. SCHWAB, A. VEIT, and K. SCHMITZ): ZP. 34, 187-228 (1900)
The course of electrolytic reduction in sulphuric acid solution of substances that are difficult to reduce.

*57) J. TAFEL (w. A. VEIT and O. SCHWAB): B. 33, 2209-2224 (1900)
The electrolytic reduction in sulphuric acid solution of substances that are difficult to reduce.

*58) J. TAFEL and M. STERN: B. 33, 2224-2236 (1900)
Reduction of succinimides to pyrrolidones.

*59) J. TAFEL and A. WEINSCHENK: B. 33, 3369-3377 (1900)
3-methyl-desoxy-xanthine and desoxy-heteroxanthine.

*60) J. TAFEL and A. WEINSCHENK: B. 33, 3378-3383 (1900)
Electrolytic reduction of methyl-uracil.

*61) J. TAFEL and A. WEINSCHENK: B. 33, 3383-3387 (1900)
Electrolytic reduction of barbituric acid.

62) J. TAFEL: B. 34, 144 (1901)
A remark on hydro-uracil (β-lactyl urea).

*63) J. TAFEL (w. O. SCHWAB and K. BOERNER): B. 34, 258-279 (1901)
Products of reduction of uric acid.

*64) J. TAFEL (w. O. SCHWAB and K. BOERNER): B. 34, 279-291 (1901)
Products of reduction of methylated uric acids.

*65) J. TAFEL and B. ACH: B. 34, 1165-1169 (1901)
Electrolytic reduction of xanthine.

*66) J. TAFEL and B. ACH: B. 34, 1170-1181 (1901)
Products of reduction of guanine.

67) J. TAFEL (w. K. BOERNER): B. 34, 1181-1184 (1901)
Tetrahydro-uric acid.

*68) J. TAFEL and K. ECKSTEIN: B. 34, 3274-3286 (1901)
Electrolytic reduction of camphoric acid imide.

*69) J. TAFEL and L. REINDL: B. 34, 3286-3291 (1901)
Electrolytic reduction of some cyclic ureides.

*70) J. TAFEL and K. NAUMANN: B. 34, 3291-3299 (1901)
K. MÜLLER

The electrolytic reduction of strychnine and brucine.

*71) J. TAFEL and K. SCHMIDT: ZE. 8, 281–288 (1902)
The reducing action of lead and mercury cathodes in sulphuric acid solution.

Cathodic polarisation in diluted sulphuric acid.

Electrolytic reduction of nitric acid in presence of hydrochloric or sulphuric acid.

*74) J. TAFEL and E. PFEFFERMANN (w. F. KOLTSCHARSCH): B. 35, 1510–1518 (1902)
Electrolytic reduction of oximes and phenylhydrazones in sulphuric acid solution.

*75) J. TAFEL and E. PFEFFERMANN: B. 36, 219–224 (1903)
Electrolytic reduction of acetyl-acetone-dioxime (dimethyl pyrazolidine).

Electrolytic reductions.

The effect of canal rays on zinc oxide. I.

The effect of canal rays on zinc oxide. II.

*79) J. TAFEL and G. FRIEDERICHS: B. 3187–3191 (1904)
Electrolytic reduction of carboxylic acids and carboxylic acid esters in sulphuric acid solution.

The polarisation during cathodic hydrogen evolution.

*81) J. TAFEL and K. NAUMANN (ptly. w. B. EMMERT): ZP. 50, 713–752 (1905)
Relationships between cathode potential and electrolytic reduction effect.

*82) J. TAFEL and B. EMMERT: ZP. 52, 349–373 (1905)
The cause of spontaneous depression of the cathode potential during electrolysis of diluted sulphuric acid.

83) J. TAFEL and H. STERN: B. 38, 1589–1592 (1905)
Diamino-succinic acid ethyl ester.

84) J. TAFEL and P. LAVACZEK: B. 38, 1592 (1905)
Thio-pyrrolidone. I.

*85) J. TAFEL and H. BUBLITZ: B. 38, 3806–3812 (1905)
Camphidones.

*86) J. TAFEL and B. EMMERT: ZP. 54, 433–450 (1906)
The electrolytic reduction of succinimide

*87) J. TAFEL (review): ZE 12, 112–122 (1906)
Cathode potential and electrolytic reduction in sulphuric acid solution.

A noteworthy way of formation of mercury alkyls.

89) J. TAFEL and O. WASSMUTH (w. B. EMMERT, ZECHENTMAYER, and STAMM): B. 40, 2831–2842 (1907)
Pyrrolidone.

*90) J. TAFEL and P. LAVACZEK: B. 30, 2842–2848 (1907)
Who was Tafel?

Thio-pyrrolidone. II.

*91) J. TAFEL and H. HAHL (w. W. JÜRGENS): B. 40, 3312-3318 (1907)
Complete reduction of benzyl-acetoacetic ester.

92) J. TAFEL: B. 40, 3318-3321 (1907)
Intermediates in chemical reactions.

93) J. TAFEL and P. A. HOUSEMAN (w. ZECHENTMAYER): B. 40, 3743-3751 (1907)
Isopuroxone.

*94) J. TAFEL and J. DODT (w. R. MAYER): B. 40, 3752-3757 (1907)
Reduction of theophylline and para-xanthine.

95) J. TAFEL and J. DODT: B. 40, 3757-3759 (1907)
Acidity of desoxy-xanthines.

*96) J. TAFEL and H. B. THOMPSON: B. 40, 4489-4497 (1907)
Electrolytic reduction of ethyl-barbituric acids.

97) J. TAFEL and R. MAYER (w. E. P. FRANKLAND): B. 41, 2546-2556 (1908)
Hydrolysis of xanthines and desoxy-xanthines.

The electrolytic reduction of hydroxylamine on copper cathodes.

Preparation of hydrocarbons by electrolytic reduction of acetoacetic esters.

100) J. TAFEL and E. P. FRANKLAND (w. K. SCHÜBEL): B. 42, 3138-3146 (1909)
Diamino-acids from desoxy-xanthines.

Electrolytic reduction of isoamyl-methyl-ketone to isohexane.

Unsaturated lead alkys.

*103) J. TAFEL and A. HERTERICH: B. 44, 1033-1034 (1911)
1-methyl-desoxy-xanthine.

*104) J. TAFEL and B. EMMERT: ZE. 17, 569-572 (1911)
The electrolytic reduction of levulinic acid and α-dimethyl-levulinic acid.

*105) J. TAFEL and W. SCHEPSS: B. 44, 2148-2154 (1911)
The electrolytic reduction of anisaldehyde.

*106) J. TAFEL (w. F. ZUBER, F. BAUER, and W. SCHEPSS): ZE. 17, 972-976 (1911)
Electrolytic reduction of ketones.

*107) J. TAFEL (w. ANDRE, W. SCHEPSS): B. 45, 437-452 (1912)
An anomaly in the reduction of acetoacetic esters.

*108) J. TAFEL: B. 45, 3321 (1912)
Formation of metal-organic compounds during electrolytic reductions.